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Method of making an organic thin film transistor and article made by the method

Abstract:

Thin film transistors in which the active layer is an ordered film of a pthalocyanine coordination compound with a field-effect mobility greater than 10<-3> cm<2>/Vs and a conductivity in the range of about 10<-9> S/cm to about 10<-7> S/cm at 20 DEG C are disclosed. Examples of suitable pthalocyanines include copper pthalocyanine, zinc pthalocyanine, hydrogen pthalocyanine, and tin pthalocyanine. Thin film devices made of these materials have an on/off ratio of at least about 10<4>. It is advantageous if the device is fabricated using a process in which the substrate is heated to a temperature in the range of about 30 DEG C to about 200 DEG C when the film is formed thereon.

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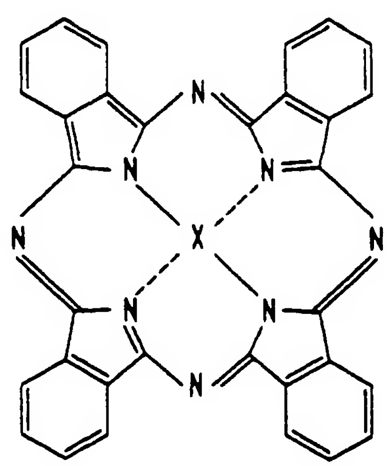
(54) Method of making an organic thin film transistor and article made by the method

(57) Thin film transistors in which the active layer is an ordered film of a pthalocyanine coordination compound with a field-effect mobility greater than 10^{-3} cm^2/Vs and a conductivity in the range of about 10^{-9} S/cm to about 10^{-7} S/cm at 20°C are disclosed. Examples of suitable pthalocyanines include copper pthalocyanine, zinc pthalocyanine, hydrogen pthalocyanine, and tin pthalocyanine. Thin film devices made of these materials have an on/off ratio of at least about 10^4. It is advantageous if the device is fabricated using a process in which the substrate is heated to a temperature in the range of about 30°C to about 200°C when the film is formed thereon.

FIG. 1



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Description

Field of the Invention

This invention relates to thin film transistors (TFTs) that contain an active layer of organic material, and to methods for making such transistors.

Background of the Invention

Organic semiconductor materials are currently being investigated for use as the active layer in a variety of devices including light-emitting diodes, nonlinear optical devices, and TFTs such as metal-insulator-semiconductor field effect transistors (MIS-FETs). Organic semiconductor materials offer processing advantages such as compatibility with flexible plastic substrates and ease of application by spin-coating and their use in processes for device fabrication is therefore attractive. However, in order for these materials to be useful for use in TFT devices, the resulting devices must have an on/off ratio (of the source/drain current) suited for the particular application. Although devices with on/off ratios as low a 100 are suited for some application, typically TFT devices must have an on/off ratio of at least about 10^3. The properties of the organic semiconductor materials that govern the on/off ratio are carrier mobility and conductivity. Organic semiconductor materials typically have a carrier mobility in excess of about 10^{-8} cm^2/Vs but less than 1 cm^2/Vs. Consequently, based upon the relationship between carrier mobility, material conductivity, and device on/off ratio, the requisite conductivity of the organic semiconductor material is defined by the carrier mobility of the material and the desired on/off ratio.

A class of doped amorphous organic semiconductors is described in Brown, A.R., et al., "A universal relation between conductivity and field-effect mobility in doped amorphous organic semiconductors," Synthetic Materials, Vol. 68, pp. 65-70 (1994). Brown et al. report a linear relationship between the conductivity and the field effect mobility of such material, i.e., as the conductivity increases so does the field-effect mobility. Although Brown et al. report materials with a very high mobility, this high mobility was achieved at the expense of conductivity. Brown et al. conclude that high on/off ratios and high mobilities are not to be expected in devices constructed from amorphous organic semiconductors. Accordingly, if satisfactory devices are to be made from these materials, the field effect mobility and the conductivity of these materials must be within a range that provides a device with an on/off ratio of at least 10^5.

SUMMARY OF THE INVENTION

The present invention is directed to a semiconductor TFT device in which the active layer is an organic semiconductor material with a field effect mobility greater than 10^{-3} $cm^2/V\text{-}s$ and a conductivity in the range of about 10^{-9} S/cm to about 10^{-7} S/cm. These organic semiconductor materials are coordination compounds of phthalocyanine (referred to herein with the abbreviation Pc) with copper, zinc, tin, or hydrogen. These coordination compounds form ordered films, and exhibit higher field effect mobility at lower conductivities than amorphous, doped pthalocyanine. The present invention is also directed to a process for making these devices.

In one embodiment of the present invention, the device is a MIS-FET type TFT with an active layer of the organic semiconductor. Such devices typically have three spaced-apart contacts (e.g. conductive metals such as gold), at least two of which are in physical contact with the semiconductor layer. The third contact is adapted to control the current through the semiconductor layer between the first and second contacts.

The TFT device of the present invention is formed on a conventional substrate material such as glass, silicon or plastic. A layer of dielectric material is formed over the substrate. One of the contacts is physically connected to the substrate and the layer of dielectric material is interposed between the other two contacts and the substrate.

In the process of the present invention, the layer of pthalocyanine coordination compound is formed on a heated substrate. The temperature of the substrate is in the range of about 30°C to about 200°C. It is advantageous if the temperature of the substrate is about 125°C to about 175°C.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of the structure of the pthalocyanine coordination compounds of the present invention wherein the ion in the pthalocyanine is indicated generally by the letter X.

FIG. 2 is a cut away side view of a TFT device of the present invention.

FIG. 3 illustrates the relationship between the field effect mobility of a Cu-Pc film and the temperature of the substrate on which the film is formed.

DETAILED DESCRIPTION

The present invention is directed to a TFT device in which the active layer is a pthalocyanine coordination compound and a process for making the device. The device of the present invention has an on/off ratio greater than 10^4 at 20°C. In order to obtain devices with the desired on/off ratio, it is advantageous if the pthalocyanine has a field effect mobility greater than 10^{-3} cm^2/V-s and a conductivity in the range of about 10^{-9} S/cm to about 10^{-7} S/cm. FIG. 1 is an illustration of a pthalocyanine coordination compound. The coordinate ion is indicated generally by the letter X. It is advantageous if the coordinate ion is either copper, zinc, tin, or hydrogen.

FIG. 2 illustrates a MIS-FET type device according to the invention. The transistor 20 is a substrate 11 over which a layer of dielectric material 13 and a metal contact 15 are formed. Two additional metal contacts, 17 and 19, are formed over the dielectric layer 13. A layer of the pthalocyanine coordination compound 21 is formed over and between the contacts 17 and 19.

The substrate of the above-described device is made of conventional materials such as silicon, glass, or plastic. The contacts are made of a conventional material for this purpose such as gold. The dielectric material is a conventional material such as silicon dioxide, silicon nitride (Si_3N_4), or aluminum oxide (Al_2O_3). The contacts and the dielectric layer are formed on the substrate using well known, conventional techniques which are not discussed in detail herein.

By way of example, MIS-FET type TFTs are formed with a 12 μm channel length and a 250 μm gate length on an n-doped silicon substrate. A 3000 Å thick layer of silicon dioxide is formed over the substrate. The silicon dioxide layer functions as a gate dielectric material and has a capacitance of about 10 nF/cm^2. Two separate gold contacts are formed over the gate dielectric layer. A film of a pthalocyanine coordination compound is formed over the gate dielectric layer and the contacts formed thereon. The pthalocyanine film is formed on a heated substrate. The temperature of the substrate is in the range of about 30° to about 200°C. It is advantageous if the substrate temperature is about 125°C to about 175°C.

The pthalocyanine film is formed on the substrate using conventional techniques such as vacuum deposition. It is advantageous if the thickness of the pthalocyanine film is about 500 Å to about 600 Å. TFTs so formed have an on/off ratio greater than 10^4 at 20°C.

Example

Pthalocyanine coordination compounds with platinum (Pt), copper (Cu), zinc (Zn), nickel (Ni), iron (Fe), tin (Sn), and hydrogen (H_2) were obtained from a commercial supplier. For convenience, the pthalocyanine coordination compound is referred to generally as X-Pc, where X is a generic designation for the coordination ion (e.g., Pt, Fe, H_2, etc.) These materials were then purified by sublimation at a pressure of less than about 8 x 10^{-4} Torr and a temperature of about 380°C . This sublimation procedure was performed three times total.

Devices were formed using the above identified pthalocyanine coordination compounds as the active layer. A layer of pthalocyanine coordination compound 21 was formed on a substrate to form the device 20 depicted in FIG. 2 and described generally above. In the context of this example, the term substrate is used to refer to the structure of a silicon substrate 11 on which is formed a layer of gate dielectric 13 with two contacts 17 and 19 formed thereon. A third contact 15 is formed directly on the silicon substrate.

The temperature of the substrate was controlled during the deposition of each film thereon to determine the effect of substrate temperature on the mobility and conductivity of the pthalocyanine layer. Individual films of each of the above-identified pthalocyanines coordination compounds were formed on substrates heated to temperatures of 30°C, 125°C, and 200°C. Each film was formed using vacuum deposition in an evaporation chamber at a pressure of 2 x 10^{-6} torr. About 50 mg of the phthalocyanine was placed in a tungsten boat. The boat was placed in a conventional evaporator system. The substrate was also placed in the evaporator on a copper block. A temperature controller was used to control the temperature of the copper block which, in turn, was used to control the temperature of the substrate. The boat was heated to a temperature of about 380°C and the pthalocyanine film was formed at a rate of about 4 Å to about 5 Å per second.

The field-effect mobility and the conductivity of the various films prepared as described above is enumerated in Table I below. The effect of the substrate temperature during film formation on the field-effect mobility and conductivity of the films is also reported in Table I.

TABLE I

Material	Property	Substrate Temperature		
		30°C	125°C	200°C
	Mobility (cm^2/Vs)	6.0 x 10^{-4}	2 x 10^{-2}	6.7 x 10^{-3}

TABLE I (continued)

Material	Property	Substrate Temperature		
		30°C	125°C	200°C
Cu-Pc	Conductivity (S/cm) on/off ratio	1.8×10^{-9} 3.7×10^{4}	4×10^{-9} 4×10^{5}	3.1×10^{-9} 1.7×10^{5}
Zn-Pc	mobility (cm^2/Vs) conductivity (S/cm) on/off ratio	2.3×10^{-4} 1.4×10^{-6} 12	2.4×10^{-3} 1.1×10^{-8} 2.2×10^{4}	2.8×10^{-3} 1×10^{-7} 2×10^{3}
H_2-Pc	mobility (cm^2/Vs) conductivity (S/cm) on/off ratio	1.3×10^{-3} 6.4×10^{-7} 160	2.6×10^{-3} 2.2×10^{-9} 8.1×10^{4}	5.6×10^{-7} 2.1×10^{-9} 26
Sn-Pc	mobility (cm^2/Vs) conductivity (S/cm) on/off ratio	7.3×10^{-5} 1.9×10^{-7} 36	3.4×10^{-3} 2.4×10^{-6} 1.6×10^{4}	not measurable 4.8×10^{-8} not measurable
Fe-Pc	mobility (cm^2/Vs) conductivity (S/cm) on/off ratio	3.6×10^{-5} 5.1×10^{-9} 570	6.9×10^{-4} 6.8×10^{-7} 110	1.1×10^{-5} 1×10^{-7} 100
Pt-Pc	mobility (cm^2/Vs) conductivity (S/cm)	1.5×10^{-4} 2.2×10^{-7}	1.5×10^{-4} 2.7×10^{-7}	9×10^{-5} 4.7×10^{-9}
	on/off ratio	120	80	2.6×10^{3}
Ni-Pc	mobility (cm^2/Vs) conductivity (S/cm) on/off ratio	7×10^{-6} 3.9×10^{-9} 120	3×10^{-5} 6.2×10^{-8} 110	5.4×10^{-5} 6.4×10^{-9} 110

The field-effect mobility reported in Table I was calculated using the following equation:

$$I_{DS}=(WC_i/2L)\mu(V_G-V_O)^2$$

where W is the channel width (250 μm), L is the channel length (12 μm) and C_i is the capacitance per unit area of the gate dielectric (10 nF/cm^2). To calculate the field effect mobility, μ, using the above-identified equation, the threshold voltage (Vo) of the device is determined from the relationship between the square root of the drain-source current (I_{DS}) at the saturated region and the gate voltage of the device (VG) by extrapolating from the measured values back to I_{DS}=0. The I_{DS} at the saturated region is determined by observing the relationship between the drain-source voltage (V_{DS}) and the drain-source current at a given V_G. I_{DS} at the saturated region is where I_{DS} no longer increases with increasing drain-source voltage. I_{DS} at the saturated region varies with V_G. This method for determining Vo is conventional and well known to one skilled in the art.

The field effect mobilities reported in Table I are average values. Devices were formed using two substrates for every material and every temperature reported in Table I. For example, devices with a Cu-Pc film were formed on six substrates total, two at each of the reported temperatures. At least twenty devices were formed on each substrate.

The on/off ratio is the ratio of the drain current (I_{D1}) flowing in saturation when V_G is equal to or greater than the drain voltage (V_D) to the I_{D2} flowing when V_G is zero. For example, if I_{DS} is 8×10^{-5} A when V_D and V_G are both -100 V and I_{DS} is 1×10^{-11} A when $V_G = 0$ and V_D -100 V, then the on/off ratio of the device is 8×10^6.

Although the inventor does not wish to be held to a particular theory, it is believed that the performance of the device is linked to the morphology of the pthalocyanine films. X-ray diffraction analysis of the films enumerated in Table I shows an increase in order in most of the films (i.e. the films became less amorphous) with an increase in the temperature of the substrate on which the films were formed. The order of the films was determined from the x-ray diffraction trace that results from the (200) lattice planes. A trace with a single peak was indicative of a highly ordered film. The intensity of this peak was observed to increase with an increase in the temperature of the substrate on which the film was formed.

Consequently, it appears that the order of the film is related to the field effect mobility of the material. As observed by the data in Table I, the field effect mobility of most films increased as the temperature of the substrate was increased

from 30° to 125°C. As noted above, the order of the film also increased with increasing substrate temperature during film formation. However, Table I also shows a decrease in field effect mobility as the substrate temperature during deposition was increased from 125° to 200°C. This effect may be explained by the fact that film discontinuities increase at higher temperatures and these discontinuities have a negative effect on field effect mobility.

The relationship between the temperature of the substrate during film formation and the field effect mobility of a Cu-Pc film is illustrated in FIG. 3. FIG. 3 demonstrates that the field effect mobility of the Cu-Pc film increases dramatically as the temperature of the substrate increases from about 30°C to about 140°C. At substrate temperatures above 140°C, the trend reverses and the field effect mobility decreases with increasing temperature.

Claims

1. A thin film transistor comprising:
   a substrate with a layer of a pthalocyanine coordination compound formed thereon and contacts for applying current through the layer of the pthalocyanine coordination compound wherein the pthalocyanine coordination compound has a field-effect mobility greater than 10^{-3} cm²/Vs and a conductivity in the range of about 10^{-9} S/cm to about 10^{-7} S/cm at 20°C and wherein the thin film transistor has an on/off ratio of the source drain current that is at least 10^4.

2. The thin film transistor of claim 1 wherein the pthalocyanine coordination compound has a coordinate selected from the group consisting of copper, zinc, hydrogen, and tin.

3. The thin film transistor of claim 2 wherein the layer of pthalocyanine coordination compound has a thickness of about 500 Å to about 600 Å.

4. The thin film transistor of claim 3 wherein the layer of pthalocyanine coordination compound is an ordered layer.

5. The thin film transistor of claim 4 wherein the thin film transistor is a MIS-FET.

6. A process for fabricating a device comprising:
   forming a layer of an ordered pthalocyanine coordination compound on a substrate heated to a temperature in the range of about 30°C to about 200°C and forming contacts on the substrate for applying current through the layer of ordered pthalocyanine coordination compound.

7. The process of claim 6 wherein the ordered pthalocyanine coordination compound is selected from the group consisting of copper pthalocyanine, zinc pthalocyanine, hydrogen pthalocyanine, and tin pthalocyanine.

8. The process of claim 7 wherein the temperature is about 125°C to about 175°C.

9. The process of claim 8 wherein the device is a thin film transistor.

10. The process of claim 9 wherein the device is a MIS-FET.

FIG. 1

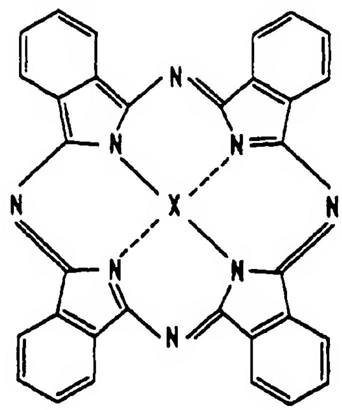

FIG. 2

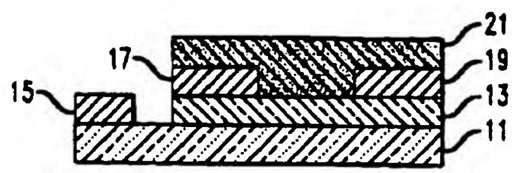

FIG. 3